

Accurate measurement of relative oscillator strengths by phase-matched nonlinear optics

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A new method for accurately measuring relative oscillator strengths is presented. The method is based on measurements of the frequencies at which a nonlinear-optical sum-mixing process is phase matched. By applying this technique to Ca I, the relative strengths of the $4s^2\ ^1S_0-4snp\ ^1P_1^0$ transitions for $n=10-13$ are measured to an accuracy of $\pm 2\%$, more than six times better than previous measurements.

The two general types of atomic spectroscopic data used by "consumers"—atomic theorists, plasma physicists, astrophysicists, etc.—are (1) atomic line positions (including shapes) and (2) atomic transition strengths or oscillator strengths (f values). Advances in tunable dye laser technology and laser spectroscopic techniques now permit measurements¹ of line positions to accuracies of greater than 1 part in 10^{11} . In contrast, f values are generally not known² to accuracies of better than 10%.

In this paper, we report on a method of accurately measuring relative f values using a nonlinear optical mixing technique. Key features of this method are (1) the relative f values are determined by frequency measurements, (2) a measurement of the light intensity is unnecessary, and (3) sample density and length, while affecting the measurement, need not be measured to get accurate f values. We have applied our technique to Ca I and measured the f values of the $4s^2\ ^1S_0-4snp\ ^1P_1^0$ transitions for $n=10, 11, 12, 13,$ and 14 , relative to the f value of the main resonance line, $4s^2\ ^1S_0-4s4p\ ^1P_1^0$. Accuracies of $\pm 2\%$ are obtained for $n=10-13$, a significant improvement over the best previous measurements³ having accuracies of $\geq \pm 12\%$.

Our method is based on the dependence of nonlinear-optical sum mixing on phase matching.⁴ The signal generated in a nonlinear-optical medium at a new frequency will, in general, maximize when the driven nonlinear polarization wave stays in phase with the wave it radiates; i.e., the process is phase matched. Beginning with Young *et al.*,⁵ various studies of nonlinear-optical mixing in atomic vapors have been carried out where a buffer gas was added or the laser frequencies were tuned to achieve phase matching.^{6,7} The aim of these studies was to maximize the signal. In contrast, Puell and Vidal,⁸ using Xe to phase-match third-harmonic generation (THG) in Rb, determined the f value of the $5s-5p$ transition in Rb I relative to the refractive index contribution of Xe. They also pointed out that relative f values for an atomic species could be obtained by us-

ing tunable lasers to phase match a nonlinear-optical sum-mixing process. It is in this spirit that the present work has been undertaken.

Our experiments were carried out using two N₂-laser-pumped dye lasers, at frequencies ν_1 and ν_2 , respectively. Typical laser intensities for the experiment were ~ 100 kW/cm² at ν_2 and ~ 30 kW/cm² at ν_1 . Laser linewidths⁹ were typically ~ 0.1 cm⁻¹. The copropagating laser beams passed through a heated pipe containing Ca and ~ 10 -torr Ne buffer gas. The heated zone was ~ 20 cm long, and a typical temperature for the measurements was 850 °C (measured at the center of the pipe), corresponding to a Ca pressure of ~ 2 torr. In the Ca vapor the visible laser beams generated a uv signal at $\nu_3=2\nu_1+\nu_2$, and this signal was recorded as ν_2 was tuned, with ν_1 held fixed. For calibration purposes and for resonant enhancement of the nonlinear susceptibility $\chi^{(3)}(\nu_3=2\nu_1+\nu_2)$, ν_1 was set at half the frequency of the $4s^2\ ^1S_0-4s5s\ ^1S_0$ two-photon transition of Ca I at 33317.3 cm⁻¹. This setting was ensured by blocking the beam at ν_2 , tuning ν_1 , and (1) looking for a maximum in the THG process due to resonance enhancement of $\chi^{(3)}(3\nu_1)$, and (2) simultaneously observing the maximum in the three-photon photoionization process. The uv was detected with a solar blind photomultiplier, and the ionization was monitored via space-charge-limited thermionic diode detection.¹⁰ With ν_1 appropriately set, light at ν_2 was added. For the transitions studied, ν_3 took on values between ~ 47650 and 48570 cm⁻¹. The $3\nu_1$ background at 49975.9 cm⁻¹ was blocked using a filter consisting of ~ 1 -cm thickness of 0.4- M KCl in H₂O. During the data runs, a small fraction of the ν_2 light passed through an air-spaced, Fabry-Perot etalon to monitor accurately the tuning of ν_2 , accomplished either by rotating the laser's diffraction grating or by placing it in a vacuum chamber and slowly admitting N₂ or Freon 14 (CF₄).¹¹ A typical data run is shown in Fig. 1. These data clearly show that the uv signal maximizes for $\nu_3 \sim 4$ cm⁻¹ below resonance with the $4s^2\ ^1S_0-4s10p\ ^1P_1^0$ transition at 47662.1 cm⁻¹, marked

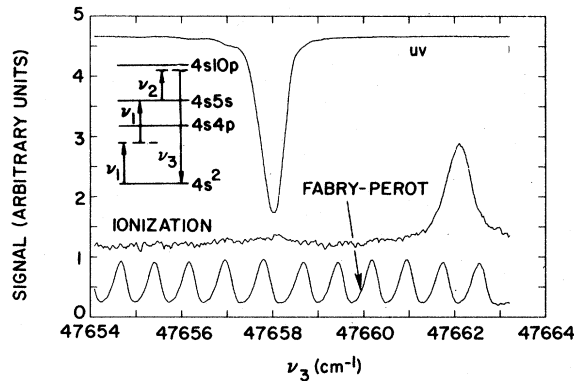


FIG. 1. Typical data with ν_3 in vicinity of $4s^2 1S_0 - 4s 10p^1 P_1^0$ transition at 47662.1 cm^{-1} . The insert on the left-hand side shows the relationship between the laser frequencies and the energy levels of Ca I.

by the maximum in the ionization signal.

In order to extract relative f -value information from this data, we take the well-known formulation⁸ for the dependence of the signal intensity, $I(\nu_3)$ on $I(\nu_1)$, $I(\nu_2)$, $\chi^{(3)}(\nu_3 = 2\nu_1 + \nu_2)$, and phase matching, namely,

$$I(\nu_3) \propto I^2(\nu_1)I(\nu_2)|\chi^{(3)}|^2(\sin\Delta kL/2)^2/(\Delta k)^2 \quad (1)$$

Here, Δk , the phase mismatch, is defined as $\Delta k = 2k_1 + k_2 - k_3$, and the vapor sample is assumed to have constant density, N , over a length L . Equation (1) is valid in the limit of plane, collinear waves, negligible linear absorption, and small signals at ν_3 . Over a small tuning range of ν_2 so that $I(\nu_2)$ is essentially constant, $I(\nu_3)$ depends on ν_2 through the dependences of $\chi^{(3)}$ and Δk on ν_2 . For ν_3 near ν_n' , we may write $\chi^{(3)}(\nu_3 = 2\nu_1 + \nu_2) \propto 1/(\nu_n' - \nu_3)$. The connection between $I(\nu_3)$ and f values comes from the dependence of k_i on the refractive indices $n(\nu_i)$, $k_i = 2\pi n(\nu_i)\nu_i$,⁹ and

$$n(\nu_i) = 1 + \frac{Ne^2}{2\pi mc^2} \left[\sum_n \frac{f_n}{\nu_n^2 - \nu_i^2} + \int \frac{df}{d\nu_c} \frac{1}{\nu_c^2 - \nu_i^2} d\nu_c \right] \quad (2)$$

In Eq. (2), e is the electronic charge, m the electron mass, and c the speed of light. Equation (2) is valid when only the atomic ground state is populated and ν_i is far enough removed from any resonance line frequency, ν_n , so that linewidth factors are negligible. The sum is over all discrete transitions, and the integral is over all continuum transitions from the ground state, $df/d\nu_c$ being the continuum density of oscillator strength. Note that even with an inhomogeneous

vapor density $N(z)$, since $\chi^{(3)}$ and Δk are both proportional to $N(z)$, it may be shown⁷ that the above formulation is still valid provided that the product NL is replaced by $\int N(z) dz$, the integration being over the entire sample length. The proportionality between Δk and $N(z)$ is contingent upon a negligible contribution to Δk from other gas atoms in the vapor, a condition readily satisfied with the use of ~ 10 -torr Ne buffer gas.

In general, the uv signal strength as a function of ν_3 depends on all f_n and $df/d\nu_c$. However, by a careful choice of frequencies, certain selected transitions may be chosen to most strongly affect $n(\nu_i)$, and the uv generation measurement will give accurate information about these transitions. For Ca I, with ν_1 and $\nu_2 \sim 14000 - 17000 \text{ cm}^{-1}$, $n(\nu_1)$ and $n(\nu_2)$ are dominated by the main resonance line, $4s^2 1S_0 - 4s 4p^1 P_1^0$, with $\nu_R = 23652.3 \text{ cm}^{-1}$ and $f_R = 1.75$.¹² In order to measure the f value, f_n , of a higher transition $4s^2 1S_0 - 4s n' p^1 P_1^0$, relative to f_R , we tune ν_3 below and near to ν_n' . When the contribution of this transition to $n(\nu_3)$, governed by the frequency offset, $\nu_n' - \nu_3$, is sufficient, phase matching may be achieved, with $I(\nu_3)$ showing a maximum as a function of ν_3 . The position of the maximum is determined primarily by the ratio f_n/f_R . However, the resonant enhancement of $\chi^{(3)}$ pulls the signal maximum from exact phase matching ($\Delta k = 0$) toward exact resonance ($\nu_3 = \nu_n'$).

The idealized situation just described, where only f_R and f_n need be considered, is not completely realized. The accuracy of the determination of f_n/f_R from the $I(\nu_3)$ vs ν_3 data depends on how accurately the other f_n and $df/d\nu_c$ are known. For the present case, using values for f_n up to $n = 17$ in the discrete sum and $df/d\nu_c$ values for higher frequencies in the continuum integral of Eq. (2),¹³ we find that the calculated phase-matching peak position shifts closer to exact resonance by 7% (of its offset from resonance) as compared to neglecting all f except f_n and f_R .

Examples of the uv signal, calculated from Eq. (1), for ν_3 near the $4s^2 1S_0 - 4s 10p^1 P_1^0$ transition, and with all relative f values taken from Geiger,¹³ are shown in Fig. 2(a). One sees that the phase-matching peak occurs $\sim 4 \text{ cm}^{-1}$ below resonance and that the peak narrows and becomes more symmetric, with the maximum moving farther from resonance as NL increases. In the limit $NL \rightarrow \infty$, the calculated curve would peak exactly at $\Delta k = 0$.

A nonlinear least-squares fit of the experimental data to Eq. (1) was carried out in order to extract relative f values for various n . The fitted parameters were f_n/f_R and NL . A typical fit is shown in Fig. 2(b) where the central maximum is seen to be fitted quite accurately. Data were taken at several temperatures so that N varied by as much as a factor ~ 10 .

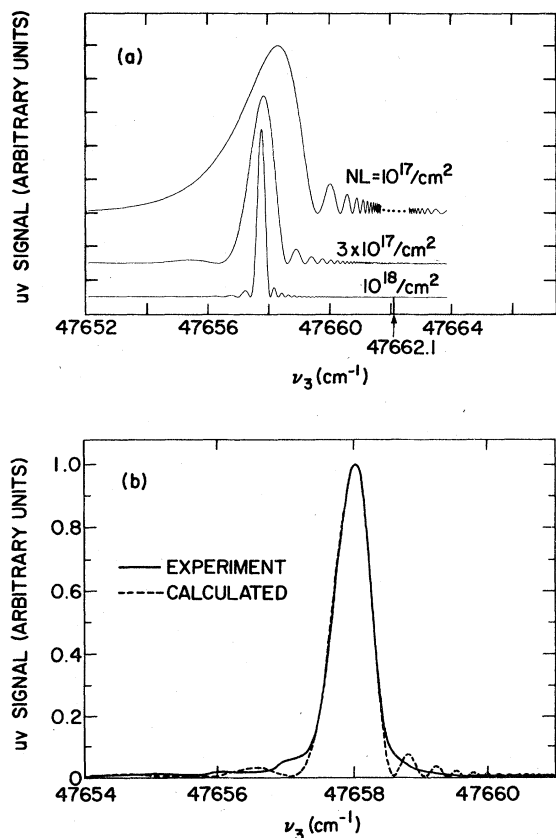


FIG. 2. uv signal as a function of ν_3 in the vicinity of the $4s^2-4s10p$ transition at 47662.1 cm^{-1} . (a) Calculated signal for three different values of NL . (b) Calculated signal (---) resulting from nonlinear least-squares fit of Eq. (1) to experimental data (—).

The values for f_n/f_R extracted from fits of data taken for a given n' showed no systematic dependence on temperature. Data at several values of Ne buffer gas pressure, from 10–200 torr, also showed no systematic dependence, as expected.

Our results are collected in Table I. The $\pm 5\%$ uncertainty listed for $n = 14$ is the standard deviation of the mean for three data runs. However, the $\pm 2\%$ uncertainty listed for $n = 10-13$ is larger than the statistical variation of several data runs for each n , reflecting the uncertainty of the other f_n and $df/d\nu_c$ values used in extracting each f_n/f_R from the data fits.¹³ For comparison purposes, Table I also lists the previously most accurate relative f values, derived

TABLE I. Ca I: relative f values $f(4s^2^1S_0-4snp^1P_1^0)/f(4s^2^1S_0-4s4p^1P_1^0)$.

n	Phase-matched nonlinear optics	Hook ^a method
10	$1.73 \times 10^{-3} \pm 2\%$	$1.85 \times 10^{-3} \pm 12\%$
11	$1.01 \times 10^{-3} \pm 2\%$	$1.17 \times 10^{-3} \pm 12\%$
12	$6.93 \times 10^{-4} \pm 2\%$	$7.89 \times 10^{-4} \pm 12\%$
13	$4.60 \times 10^{-4} \pm 2\%$	$4.98 \times 10^{-4} \pm 15\%$
14	$3.7 \times 10^{-4} \pm 5\%$	$3.95 \times 10^{-4} \pm 23\%$

^aParkinson *et al.*, Ref. 3.

from Hook measurements.³ In each case, our measurement falls within the error range of the values given by Parkinson *et al.*,³ but always toward the lower end of the range. At this time, we have no explanation for the $\sim 10\%$ systematic difference between results of the two types of measurements.

In summary, we have demonstrated a new method of determining relative f values in atomic vapors, which, when applied to Ca I, yields values at least six times more accurate than previous measurements. The precision is limited by inaccuracies in the experimental values of other resonance line transitions. By applying this technique to more members of the $4s^2-4snp$ series, a self-consistent set of f values accurate to better than $\pm 1\%$ should be obtainable. Such precision would be welcomed by solar physicists trying to determine the abundance of Ca in the photosphere of the sun and theoreticians calculating f values for Ca. A further advantage of this method is its capability of measuring f values for uv transitions using only visible and near-infrared laser light. Applications to transitions in atoms other than Ca I, including ions, and to excited-state-excited-state transitions are under consideration.

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